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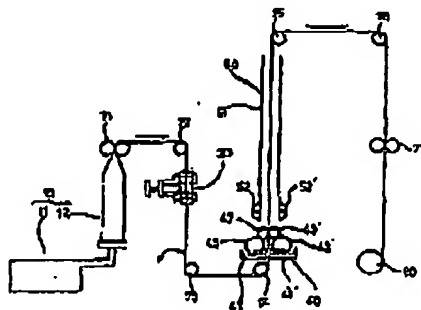
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[54] 发明名称 农业及园艺用无水滴合成树脂薄膜制造方法及其制造设备

[57] 摘要

本发明涉及一种农业及园艺用无水滴合成树脂薄膜的制造方法及其制造设备,由压延输出装置、薄膜表面活性化装置、无水滴剂涂覆装置、垂直形干燥器和薄膜卷轮构成的制造设备,对压延输出的合成树脂薄膜的表面进行活性化处理,然后涂覆由胶状二氧化硅和水性丙烯酸类树脂组成的无水滴剂,并进行干燥制成无水滴合成树脂薄膜。该方法可增强无水滴剂的耐久性、降低制造费用,其制造设备简单、使用安全,无空气污染,不受薄膜宽度限制。



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# 权 利 要 求 书

1、一种农业及园艺用无水滴合成树脂薄膜的制造方法，其特征在于利用稀释氟气对压延输出的合成树脂薄膜的表面进行活性化处理，在此活性化薄膜表面上涂覆由胶状二氧化硅和水性丙烯酸类树脂组成的无水滴剂，并进行干燥，制成无水滴合成树脂薄膜。

2、根据权利要求1所述的制造方法，其特征在于氟气采用空气、氮气、氦气、二氧化碳、氩气中的一种或一种以上的气体稀释，氟气浓度稀释至1-5%时使用。

3、根据权利要求1所述的制造方法，其特征在于无水滴剂是在水、酒精分散介质中混入胶状二氧化硅和水性丙烯酸类树脂，其总固形粉含量为0.1-35%重量份。

4、根据权利要求1所述的制造方法，其特征在于无水滴剂中的胶状二氧化硅和水性丙烯酸类树脂的比例为1:4-3:1。

5、一种农业及园艺用无水滴合成树脂薄膜的制造设备，其特征在于由压延输出装置、薄膜表面活性化装置，无水滴剂涂覆装置，垂直形干燥器和薄膜卷轮构成，薄膜表面活性化装置的直六面体外壳上、下端设置有细长入口和出口，其宽度方向两侧对应排列有氟气供应管。

6、根据权利要求5所述的制造设备，其特征在于直六面体外壳的细长入口和出口的侧面设置氟气吸收箱，箱两侧导管连接到集合管上，集合管上连接了设置有引风机的导管，该导管的出口端设置净化器。

## 说 明 书

## 农业及园艺用无水滴合成树脂薄膜制造方法及其制造设备

本发明涉及一种农业及园艺用无水滴合成树脂薄膜制造方法及其制造设备。

农业及园艺用温室可以采用较大块的玻璃板或丙烯酸树脂板材为披覆材料，但是一般为了节省投资采用合成树脂薄膜，比如塑料薄膜为披覆材料。上述的合成树脂薄膜通常是指聚烯烃类树脂，聚氯乙稀树脂，乙烯醋酸树脂等。

但是，上述的合成树脂薄膜具有表面疏水性，温室中的空气和土壤中所含的水蒸气凝结到薄膜的里侧形成水滴，妨碍太阳光线的透过，不利于温室内部温度的上升，不利于温室内部的农作物的成长；并且水滴滴到农作物上引起冷害；另外，水滴淋湿人的衣服引起不适感。

因此，使用疏水性合成树脂薄膜时，应给薄膜的表面形成亲水性，来克服上述缺点。

给予合成树脂薄膜表面亲水性的方法，分为制造合成树脂薄膜时添加无水滴剂的方法（内含无水滴剂薄膜）和在薄膜表面涂覆无水滴剂的方法（无水滴剂涂覆形薄膜）。

上述的内含无水滴剂薄膜的制造方法刊登在日本国特许专利公开 6-93139 号公报上，此薄膜是把多价乙醇及羟类硬脂酸的酯（A 成分）成分和多价乙醇脂肪酸酯类防雾剂（B 成分）按照 A：B=80~20：20~80 的比例混合的聚乙稀类树脂。

另外，上述的无水滴剂涂覆形薄膜制造方法刊登在韩国特许专利公开第 1988-11241 号、第 1995-25056 号、第 1996-34359 号等文献上。上述韩国特许专利公开第 1988-11241 号上介绍了在聚乙烯薄膜表面上，经过电晕放电处理后涂覆亲水性高分子材料（藻朊酸钠）并进行干燥的农业用及包装用高分子薄膜的制造方法。韩国特许专利公开第 1995-25056 号上介绍了在薄膜的表面上，经过电晕放电处理后涂覆无水滴剂（界面活性剂）稀释溶液

并进行热风烘干的农业用合成树脂薄膜的无水滴剂涂覆方法。韩国特许专利公开第 1996-34359 号上介绍了把在 100 个含量单位分散介质中混合胶状氧化铝 0.1~5 重量单位、胶状二氧化硅 0.01~1 重量单位、阴离子性界面活性剂 0.001~0.1 重量单位和无机层状化合物 0.005~0.5 重量单位而构成的组成物涂覆在合成树脂薄膜上的农业用薄膜。

但是，上述的内含无水滴剂形薄膜，因为其内含的无水滴性界面活性剂渐渐溶出而发挥其亲水性，所以界面活性剂慢慢流失，另外也因此要增加其添加量，从而不利于太阳光线的透过。

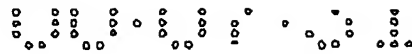
另外，上述的无水滴剂涂覆形薄膜的太阳光线虽透过性优良，但是因为把无水滴剂分散到水、酒精等分散介质上，所以其无水滴剂和薄膜之间的结合力较弱。为此，涂覆之前为把薄膜表面活性化，进行电晕放电处理。此时使用高电压，所以较危险，并且还产生大量的臭氧气体而严重污染空气，对操作者的健康不利；另外它需要电极、高频发生器等设备，投资较大，制造宽薄膜时受限制。

本发明的目的是提供一种农业及园艺用无水滴合成树脂薄膜的制造方法及其制造设备。该方法能克服已有技术缺点，可增强无水滴剂的耐久性、降低制造费用；其制造设备简单、使用安全，无空气污染，投资少、不受薄膜宽度限制。

本发明的目的是这样实现的：该方法是利用稀释氟气对压延输出的合成树脂薄膜的表面进行活性化处理，在此活性化了的薄膜表面上涂覆由胶状二氧化硅和水性丙烯酸类树脂组成的无水滴剂，并进行干燥，制成农业及园艺用无水滴薄膜。

该制造设备由压延输出装置、薄膜表面活性化装置、无水滴剂涂覆装置、垂直形干燥器和薄膜卷轮构成。薄膜表面活性化装置的直六面体外壳上、下端设置有细长入口和出口，其宽度方向两侧设置有氟气供应管。

上述合成树脂薄膜通常以可燃性树脂即聚氟乙烯树脂、聚醋酸乙烯树脂、聚酯树脂、聚烯烃类树脂等制造。上述聚烯烃类树脂使用聚乙烯树脂、



聚丙烯树脂，且上述薄膜包含各种填充剂、紫外线稳定剂等。

上述的氟气与薄膜表面的氢原子反应，从而产生氟化氢并产生碳素基体，此碳素基体与另外的氟原子结合或以基体状态存在一定时间。

如上所述，氟气破坏薄膜表面的均匀氢原子状态，使其形成不均匀状态，从而增加薄膜表面的附着能力，因此能够使后述的由胶状二氧化硅和丙稀基树脂组成的无水滴剂牢固地附着在薄膜的表面。

另外，因上述的氟气的反应能力太强，为防止薄膜的性质发生变化，用空气、氮气、氩气、二氧化碳、氢气中的一种或一种以上的气体，把氟气稀释到 1~5% 的浓度使用，如超过此浓度薄膜表面的活性降低。

上述的无水滴剂是在水、酒精等分散介质中混入胶状二氧化硅和水性丙稀基树脂组成的，其中胶状二氧化硅和水性丙稀基树脂的比例为 1:4~3:1，使无水滴剂中的总固形物含量达到 0.1~35% 重量份。应保持上述比例从而使薄膜和胶状二氧化硅的附着力较大，同时，也保持良好的亲水性。

上述无水滴剂中使用的亲水剂除包括用  $\text{SiO}_2$  表示的二氧化硅之外也包括无水硅酸或硅酸，此胶状二氧化硅具有玻璃一样的高透明度，尤其是在水湿状态下通常是以 8~12  $\mu$  的微细粒子分布，因此适合于和下述的附着剂混合使用，并更加透明，所以是一种非常优良的亲水剂。

另外，上述的胶状二氧化硅本身不具有附着力，因此把薄膜表面用氟气处理，同时与耐光性和耐水性良好的水性丙稀基类树脂附着剂混合使用，从而增加薄膜和亲水剂之间的附着力，增强无水滴剂的耐久性。

以下结合附图和实施例对本发明作进一步描述。

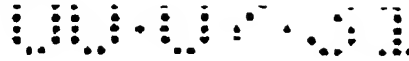
图 1 是本发明的无水滴合成树脂薄膜制造设备的一种结构示意图。

图 2 是图 1 中薄膜表面活性化装置的放大结构示意图。

图 3 是图 1 中干燥器的局部放大结构示意图。

图 4 是本发明无水滴剂涂覆装置的另一种结构示意图。

根据图 1-4 详细说明本发明的具体结构和实施方法。该装置由压延输出装置、薄膜表面活性化装置、无水滴剂涂覆装置、垂直形干燥器和薄膜卷轮



构成。其中 10 是压延输出装置，由压延机 (11) 和定形输出器 (12) 组成。20 是对在上述压延输出装置 (10) 上形成的合成树脂薄膜 (F) 的表面进行活性化的表面活性化装置。此薄膜表面活性化装置 (20) 的直六面体外壳 (21)，上、下端设置有细长入口 (22) 和出口 (23)，外壳 (21) 的宽度方向两侧以一定间距对应排列有氟气供应管 (24)、(24')，把氟气通过 (24)、(24') 喷射到薄膜 (F) 的两面，从而进行表面活性化。另外，在外壳 (21) 的入口 (22) 和出口 (23) 的侧面设置氟气吸收箱 (25)、(25')，其两侧连接导管 (26)、(26')、(27)、(27')，并把 (26)、(26')、(27)、(27') 连接到集合管 (28) 上，此集合管 (28) 上连接了设置有引风机 (30) 的导管 (29)，此导管 (29) 的出口端设置了净化器 (31)。在往薄膜两面喷射稀释氟气进行表面活性化时，通过机壳 (21) 的入口 (22) 和出口 (23) 吸入未反应的剩余氟气并进行净化。40 是无水滴剂涂覆装置，薄膜 (F) 从无水滴剂贮存槽 (41)、(41') 之间通过，贮存槽 (41)、(41') 上设置有无水滴剂输送轮 (42)、(42')，与此输送轮 (42)、(42') 相应接触处设置有涂覆轮 (43)、(43')，薄膜在经过涂覆轮 (43)、(43') 之间时其表面被涂覆无水滴剂。上述无水滴剂涂覆装置 (40) 可以设置成图 1 所示的状态，也可以设置成图 4 所示的在贮存槽 (410) 里设置输送轮 (420) 的浸泡涂覆状态。50 是垂直形干燥器，在直六面体外壳 (51) 中通过其两表面被无水滴剂涂覆装置 (40) 涂覆有无水滴剂的薄膜 (F)，并用热风干燥无水滴剂。在上述外壳 (51) 的下端设置有其上连接热风供应管 (53)、(53') 的热风分配室 (52)、(52')，室内有往薄膜输送方向送热风的热风喷射孔 (54) (54')，此孔往薄膜输送方向倾斜，以防止热风吹到无水滴剂涂覆装置 (40) 方向。因此可以避免涂覆轮 (43)、(43') 被无水滴剂涂覆、贮存槽 (410) 中的无水滴剂被吹干和薄膜 (F) 被软化而产生皱纹等现象。上述干燥器 (50) 的高度根据压延输出装置的输出速度而决定，实际输出速度为 15~20m/分钟时，干燥器 (50) 的高度定为 3 米左右。另外，上述热风分配室 (52) (52') 在图 1 中只显示一组，但可根据具体情况设置多个组。60 是薄膜卷轮，在干燥器 (50) 中



完成干燥工序的薄膜用卷轮 (60) 卷起来, 以便存放和运输薄膜 (F)。

未说明符号 71、72、73、74、75、76 是导轮, 77 是引胀轮。

如上所述的本发明无水滴合成树脂薄膜制造设备, 在压延输出装置 (10) 压出薄膜 (F), 此薄膜 (F) 经过薄膜表面活性化装置 (20) 时, 被通过氟气供应管 (24) (24') 喷射到薄膜表面的 1~5% 稀释氟气活性化, 并增强表面附着能力。

在薄膜表面活性化装置 (20) 中进行活性化作业时, 通过入口 (22) 和出口 (23) 泄漏的未反应剩余氟气, 被收集到氟气吸收箱 (25)、(25') 中, 此氟气与吸收到的空气一起被吸收引风机 (30) 经过导管 (26)、(26')、(27)、(27') 收集到集合管 (28) 中并净化。

表面被活性化的薄膜 (F) 通过无水滴剂涂覆装置 (40), 其表面涂覆一定厚度的无水滴剂, 然后通过 40℃~70℃ 的干燥器 (50) 干燥。热风通过热风供应管 (53)、(53') 到达外壳 (51) 下端的热风分配室 (52)、(52'), 并通过喷射孔 (54)、(54') 顺着薄膜 (F) 的输送方向烘干涂覆在薄膜表面的无水滴剂, 由此制成无水滴薄膜。

上述的无水滴合成树脂薄膜的制造设备, 在压延输出装置 (10) 的后面直接连上无水滴化装置, 从而直接制造无水滴薄膜。另外, 也可以仅用无水滴化装置把现有的非无水滴薄膜变成无水滴化薄膜。

#### 实施例 1

厚度为 60 $\mu$ , 宽度为 32cm 的聚乙烯稀薄膜, 以 2m/分的速度通过表面活性化装置, 采用重量各为 0.5g 的胶状二氧化硅和丙稀基类树脂混合到 1L 水中的无水滴剂, 用浸泡涂覆法 (图 4) 涂覆表面, 并在 60℃ 温度的干燥器中干燥。此薄膜的无水滴剂涂覆量为 0.2g/m<sup>2</sup>。

#### 实施例 2

厚度为 60 $\mu$ , 宽度为 32cm 的聚乙烯稀薄膜, 以 5m/分的速度通过表面活性化装置, 采用重量各为 1.5g 的胶状二氧化硅和丙稀基类树脂混合到 1L 水中的无水滴剂, 用导轮涂覆法涂覆 (图 1) 表面, 并在 70℃ 温度的干燥器中



干燥。此薄膜的无水滴剂涂覆量为  $0.5\text{g}/\text{m}^2$ 。

### 比较例 1

采用和实施例 2 相同的材料和方法，其中使用醋酸乙稀基类附着剂代替了丙稀基类树脂制造了无水滴薄膜。

### 实验分析

用实施例 1、2 和比较例 1 的方法制造的无水滴薄膜，在  $60^\circ\text{C}$  恒温的水槽上进行了实验，其结果如表 1 所示。如表所示，本发明制造的无水滴薄膜长时间保持了良好的无水滴性能。

## 实验结果

表 1

时间 类别	1 天	10 天	30 天	60 天	180 天	360 天
实施例 1	⊙	⊙	⊙	0	0	×
实施例 2	⊙	⊙	⊙	⊙	⊙	⊙
比较例 1	⊙	0	△	×	×	×

注：⊙：完全无水滴

0：1/5 的表面形成水滴

×：表面的 1/2 形成水滴

如上所述，本发明的无水滴合成树脂薄膜的制造方法，用稀释氟气活性化处理薄膜的表面，把胶状二氧化硅亲水剂用丙稀基类树脂附着剂牢固地涂覆到薄膜的表面，因此增强了无水滴剂的耐久性，其无水滴性能一直能维持到薄膜的使用寿命结束为止。另外，此种薄膜不存在无水滴剂的溶出现象，对农业及园艺作物和土壤没有危害，其生产成本也比较低。

本发明的无水滴合成树脂薄膜的制造设备，利用氟气进行薄膜表面的活



W. V. S. J.

性化处理，因此使用安全，设备简单、投资少，也可以较容易地制造宽幅薄膜。另外，此设备可以把生产中产生的未反应剩余氟气吸收并净化，因此，也不存在空气污染的问题。

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说明书附图

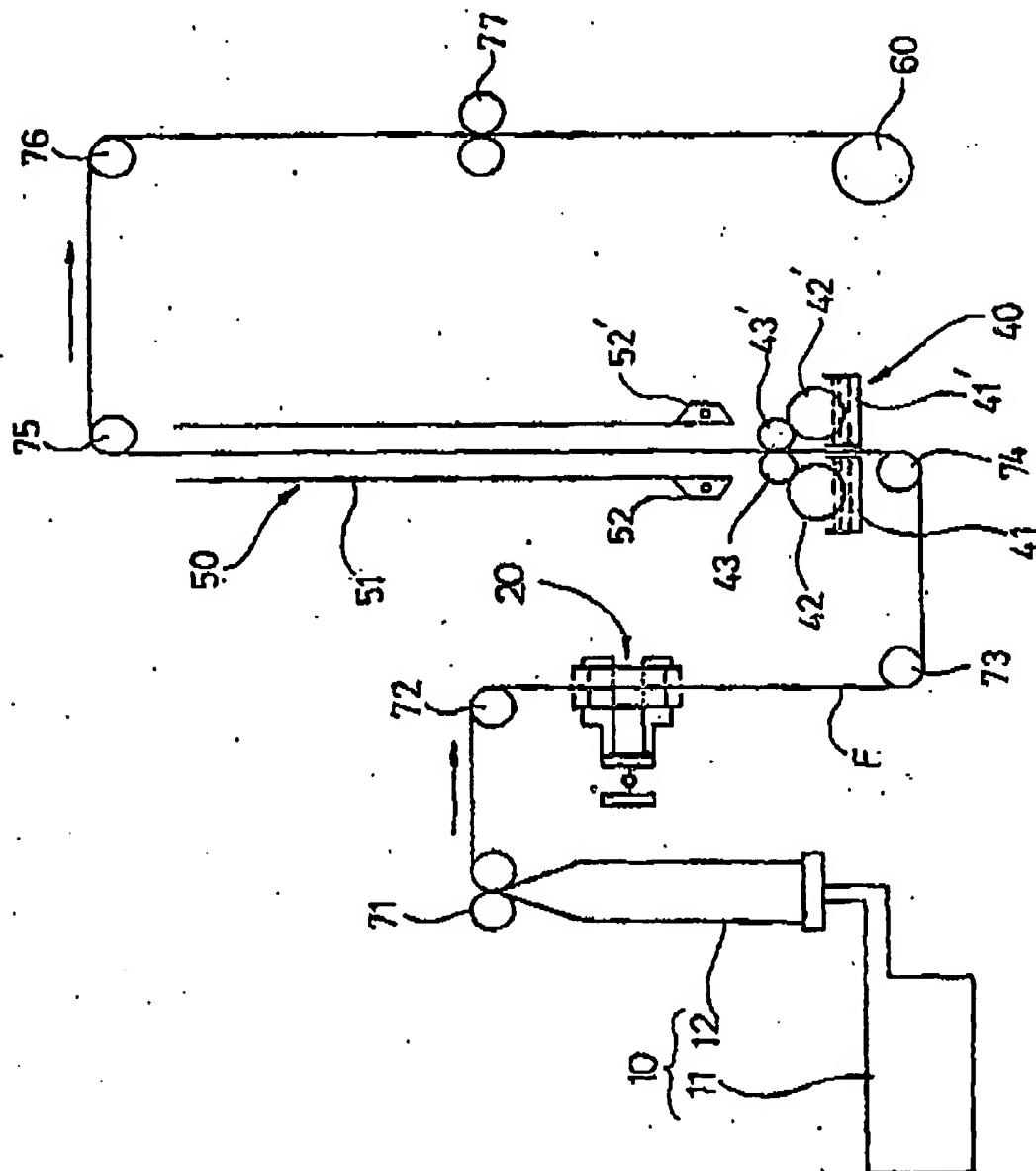


图 1

00-04-01

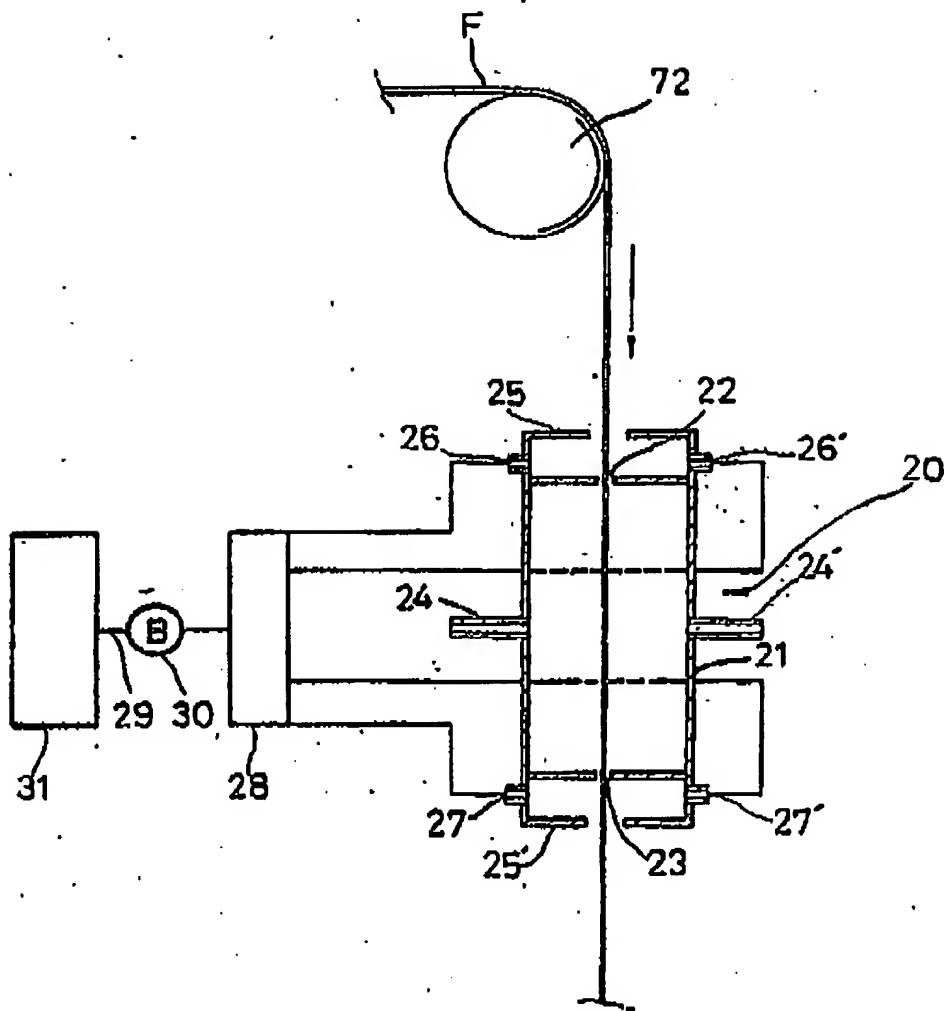


图 2

00.00.31

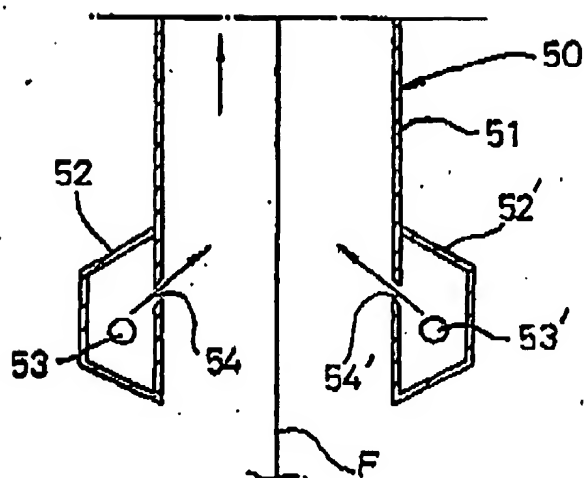


图 3

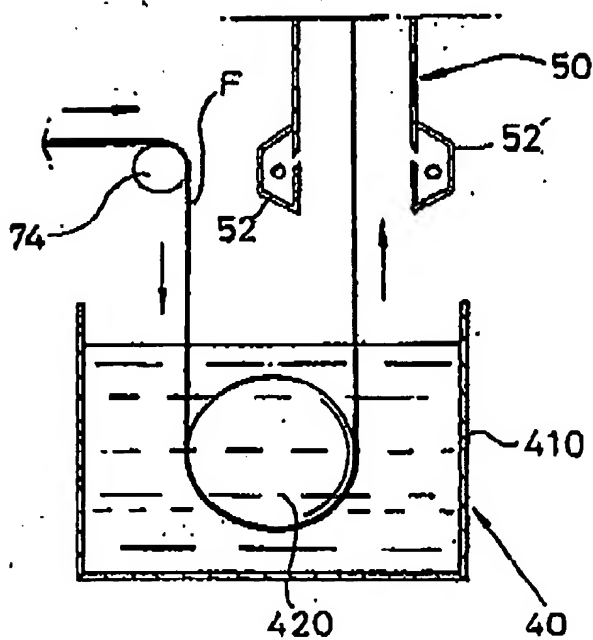


图 4



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## 第一次审查意见通知书正文

申请号: 038A4552.7

如说明书所述, 本申请涉及一种氧氟化。经审查, 现提出如下审查意见。

1、新提交的权利要求 10 和说明书第 6 页第 3 行的内容超出了原说明书和权利要求书记载的范围, 从而导致该权利要求和说明书不符合专利法第 33 条的规定。在原始公开的文本中并没有提及“暴露于氧氟化气氛中的固体表面是干燥的”, 因此该修改超出了原始公开的范围。

2、权利要求 2 得不到说明书的支持, 不符合专利法第 26 条第 4 款的规定。在本申请的所有实施例中提及的活化材料均为聚合物纤维、水泥等, 并没有具体提及碳作为活化材料, 且碳的表面与这些材料存在本质的区别, 因此仅由上述实施例很难判断本发明的氧氟化能在碳材料的表面进行, 因此其得不到说明书的实质性支持。

3、权利要求 1 不具备新颖性, 不符合专利法第 22 条第 2 款的规定。对比文件 1 (CN1336281 A) 公开了一种农业及园艺用无水滴合成树脂薄膜的制备方法及其制造设备, 并具体公开了以下的技术特征“一种农业及园艺用无水滴合成树脂薄膜的制造方法, 其特征在于利用稀释氟气对压延输出的合成树脂薄膜的表面进行活性化处理; 氟气采用例如空气、氟气 (其中包含氧气和水蒸汽, 与本发明的实施例相对应) 等中的一种或一种以上其它进行稀释, 氟气浓度稀释至 1-5%。”，并进一步公开了具有直六面体外壳, 可以让薄膜连续通过进行活化的薄膜表面活性化装置 (参见该对比文件的权利要求 1-6、说明书第 3 页最后 1 段—第 5 页第 4 段和附图 2)。该权利要求所要求保护的技术方案与该对比文件所公开的内容相比, 所



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不同的仅仅是文字表达方式上略有差别，其技术方案实质上是相同的，且两者属于相同的技术领域，并能产生相同的技术效果，因此该权利要求不具备新颖性。

4、从属权利要求 3-7、9 的附加技术特征已经在对比文件其中公开（参见该对比文件的权利要求 1-6），因此当其引用的权利要求不具备新颖性时，它们也不具备专利法第 22 条第 2 款规定的新颖性。

5、从属权利要求 8、11-12 的附加技术特征虽然没有在对比文件 1 中公开（对比文件 1 的活化时间是通过活化装置的速度来表示的），但这种活化处理时间、以及对被活化材料的表面清洁处理都属于本领域的公知常识，因此，当其引用的权利要求不具备新颖性时，其不具备专利法第 22 条第 3 款规定的创造性。

基于上述理由，本申请的独立权利要求以及从属权利要求都不具备新颖性或创造性，同时说明书中也没有记载其他任何可以授予专利权的实质性内容，因而，本申请不具备被授予专利权的前景。

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CLAIMS: 1PAGE; DESCRIPTION: 7 PAGES;  
DRAWINGS: 3 PAGES

[54] TITLE OF INVENTION: Method and Equipment For Producing Water-Drop-Free Synthetic Resin Film For Agriculture and Gardening Use

[55] Abstract:

The present invention relates to a method of equipment for producing a water-drop-free synthetic resin film for agriculture and gardening use. Said equipment is composed of a calendering and conveying device, a film surface activating device, a water drop resistant coating device, a vertical drier and a film coiling wheel. The surface of synthetic resin film is activated, then coated with a water drop resistant which is composed of colloidal silicon dioxide and an aqueous propenyl resin, further subjected to drying to obtain the water-drop-free synthetic resin film of the present invention. The method has the following advantages: improved durability of the water drop resistant, low cost, simple equipments, no air pollution, no limit to the film width.



### Method and Equipment For Producing Water-Drop-free Synthetic Resin Film For Agriculture and Gardening Use

The present invention relates to a method and equipment for producing a water-drop-free synthetic resin film for agriculture and gardening use.

The greenhouse for agriculture and gardening use is usually is covered by large glass or acrylic resin sheets. For the sake of low cost, the greenhouse may be covered by a synthetic resin film, such as a plastic film. The synthetic resin includes polyolefin resin, polyvinylchloride resin, vinyl acetate resin, and the like.

Nevertheless, the synthetic resin film has a hydrophobic surface, so the moisture contained in the air and soil in the greenhouse may be condensed onto the inner surface of the film to form water drops. The water drops will prevent sunlight from passing through the film, retard the rise of the temperature and the growth of the crops in the greenhouse, and harm the crops when dripped onto it. Besides, the clothes wetted by the water drops are not comfortable.

Therefore, it is necessary to make the surface of the hydrophobic synthetic resin film hydrophilic, so as to overcome said defects.

Imparting hydrophilicity to the surface of a synthetic resin film may be conducted by adding a water drop resistant into the synthetic resin film during production (a film containing a water drop resistant) or by applying a water drop resistant to the surface of the film (a film coated by a water drop resistant).

A method for producing a film containing a water drop resistant is disclosed in JP Patent Publication No. 6-93139. The film is made by a polyethylene resin doped with an agent prepared by combining at least one hydroxystearate of a polyhydric alcohol (A) with at least one fatty acid ester of a polyhydric alcohol (B) in a ratio of component A to component B of 80/20 to 20/80.

In addition, methods for making a film coated by a water drop resistant are disclosed in Korea Patent Publication Nos. 1998-11241, 1995-25056, 1996-34359 and et al. Korea Patent Publication No. 1998-11241 discloses a method for making a high molecular film for agriculture and package use comprising corona discharging a surface of a polyethylene film, applying a hydrophilic polymer material, such as sodium alginate, to the corona discharged surface of the film and drying the film. Korea Patent Publication No. 1995-25056 discloses a method for making a water-drop-free synthetic resin film comprising corona discharging a surface of a film,

applying a dilute solution of a water drop resistant (surfactants) to the corona-discharged surface of the film, and drying the film by hot air. Korea Patent Publication No. 1996-34359 discloses a process for applying a composition comprising 0.1 to 5 parts by weight of colloidal alumina, 0.01 to 1 parts by weight of colloidal silica, 0.001 to 0.1 parts by weight of anionic surfactants, and 0.005 to 0.5 parts by weight of an inorganic lamellar compound dispersed in 100 parts by weight of a medium, to a synthetic resin film for agriculture use.

However, since the film containing a water drop resistant exhibits hydrophilicity by gradually exuding the contained a water-drop-free surfactant, the surfactant will be slowly washed away. Thus, the amount of the surfactant shall be increased, but it may impede sunlight to pass through.

On the other side, although the film coated by a water drop resistant has a good sunlight transmittivity, there is a weak bonding between the film and the water drop resistant because the agent is dispersed into a medium, such as water or alcohol. In order to enhance the bonding, the surface of the film is activated by corona discharge prior to coating. Since the corona discharge is conducted at a high voltage, it is very dangerous. In addition, the corona discharge will produce much ozone which will heavily pollute air and harm the health of the operator. Furthermore, the investment expenditure is very high because it needs a lot of equipments, such as electrodes, high-frequency generator, and the like. Moreover, it is difficult to make a wide film by this method.

The purpose of this invention is to provide a method and equipment for producing a water-drop-free synthetic resin film for agriculture and gardening use. The method of the present invention can overcome the technical defects of the prior art, improve the durability of the water drop resistant, reduce the manufacturing cost, use simple equipments. Moreover, the method is safe, cost effective, without air pollution, and can make a wide film.

The purpose of the present invention is achieved by a method comprising activating the surface of a calendered synthetic resin film with diluted fluorine gas, applying a water drop resistant composed of colloidal silicon dioxide and an aqueous propenyl resin to said activated surface of the film, and drying the film, to form a water-drop-free synthetic resin film.

The equipment for carrying out the method comprising a calendering and conveying device, a film surface activating device, an applicator for the water drop

resistant, a vertical drier, and a film coiling wheel, said film surface activating device comprising a vertical hexahedral shell having a slot inlet on the top and a slot exit on the bottom of the shell, and fluorine supply pipes arranged on the both sides of the shell in a traverse direction.

The synthetic resin film is usually made from an inflammable resin, such as polyvinyl chloride, polyvinylacetate, polyester, or polyolefin. The polyolefin resin includes polyethylene resin and polypropylene resin. In addition, the film contains various filler, UV-stabilizer, and the like.

Fluorine reacts with the hydrogen atom on the surface of the film to produce hydrogen fluoride and a carbon-based substrate which, in turn, bonds to other fluorine atoms or exists as it is for a given period.

As described above, fluorine destroys an uniform state of the hydrogen atoms on the surface of the film so as to form a non-uniform state of the hydrogen atoms and enhance the adhesion of the film surface. As a result, a water drop resistant composed of colloidal silicon dioxide and propenyl resin can firmly adhere to the treated surface of the film.

Besides, because fluorine is very reactive, it is diluted to a concentration of 1 to 5 % by weight with one or more gas selected from the group consisting of air, nitrogen, argon, carbon dioxide and helium so as not to change the property of the film. If the concentration is beyond the range, the surface of the film will deteriorate.

The water drop resistant is formed by dispersing colloidal silicon dioxide and an aqueous propenyl resin in a medium, such as water or alcohol, wherein the ratio of colloidal silicon dioxide to the aqueous propenyl resin is in a range of 1:4 to 3:1. The water drop resistant has a total solid content of 0.1 to 35 % by weight. If said ratio falls within the above range, there are a good hydrophilicity and a strong adhesion between the film and colloidal silica.

In addition to  $\text{SiO}_2$ , the hydrophilic agent used in the water drop resistant includes silicic acid anhydride or silicic acid. The colloidal silica has a high transparency, like glass, and usually has a particle size distribution of from 8 to 12 microns, especially in a wet state. Thus, such colloidal silica can be mixed with the following adhesive and it will be more transparent. Therefore, it is a very good hydrophilic agent.

Besides, since said colloidal silica has no cohesion, the bonding between a film and the hydrophilic agent and the durability of the water drop resistant are improved

by treating the surface of the film with fluorine and combining the colloidal silica with a light and water fast aqueous propenyl resin adhesive.

The present invention will be in detail described with reference to the following drawings and examples.

FIG 1 is a schematic view of an equipment of producing a water-drop-free synthetic resin film of the present invention;

FIG 2 is a partial enlarged schematic view of the device for activating a film surface as shown in FIG 1;

FIG 3 is a partial enlarged view of the drier as shown in FIG 1;

FIG 4 is a schematic view of a device of applying the water drop resistant.

As shown in FIG 1 to 4, the equipment of the present invention comprises a calendering and conveying device, a film surface activating device, an applicator for the water drop resistant, a vertical drier, and a film coiling wheel. The calendering and conveying device 10 consists of calender (11) and shaper (12). The film surface activating device (20) activates the surface of the synthetic resin film (F) formed in the calendering and conveying device (10). The film surface activating device (20) has a vertical hexahedral shell (21) having a slot inlet (22) on the top and a slot exit (23) on the bottom of the shell, and fluorine supply pipes (24), (24') arranged on the both sides of the shell in a traverse direction. Fluorine is sprayed onto the both sides of the film (F) through the pipes (24), (24') and activates the surface of the film. Fluorine collection chambers (25), (25') are installed around the inlet (22) and the exit (23) of the shell (21). Pipes (26), (26'), (27) and (27') are arranged on the both sides of the fluorine collection chambers (25), (25') and communicated with a collector pipe (28) which is connected to the pipe (29) of an exhaust fan (30). The exit of the pipe (29) is equipped with a decontaminator (31). While the surface of the film is activated by spraying diluted fluorine onto the both side of the film, the unreacted fluorine escaping from the inlet (21) or the exit (22) of the shell (21) is collected and decontaminated. 40 represents an applicator for an water drop resistant. The film (F) is passed through the reservoirs (41), (41') for the water drop resistant, on which feed rolls (42), (42') for the water drop resistant is equipped. Coating rolls (43), (43') are installed at the contact between feed rolls (42), (42'). While the film (F) passes through the coating rolls (43), (43'), the water drop resistant is applied thereto. The applicator (40) for the water drop resistant may be configured as shown in FIG 1 or 4. In FIG 4, feed roll (420) is immersed in the reservoir (410). 50 represents a vertical

drier. The film (F) coated by the water drop resistant in the applicator (40) is passed through a vertical hexahedral shell (51) and dried by hot air. Hot air dispensing chambers (52), (52') equipped with hot air feed pipes (53), (53') are installed at the lower ends of the shell (51). The chambers have hot air jet nozzles (54), (54') toward the film conveying direction so as to prevent hot air from blowing toward the applicator (40). In this way, the evaporation of the water drop resistant in the reservoir (410) and the shrinkage of the film may be avoided. The height of the drier (50) depends on the conveying speed of the calendering and conveying device. When the conveying speed of the film is in a range of about 15 to 20 m/min., the drier (50) is 3 m high. FIG 1 shows only one set of hot air dispensing chambers (52), (52'), but more than two sets of the chambers may be installed, if desired. 60 represents a film coiling wheel. The dried film is coiled by the coiling wheel (60) so as to be stored and transported.

The not explained signs 71, 72, 73, 74, 75, 76 represent guide wheels. Sign 77 represents a pair of driving wheels.

In the above-described equipment for producing a water-drop-free synthetic resin film of the present invention, the calendering and conveying device (10) calenders a film (F). When the film (F) is passed through a film surface activating device (20), it is activated by 1 to 5% of diluted fluorine sprayed onto the surface of the films through fluorine feed pipes (24), (24'). Fluorination improves the adhesion of the surfaces of the film.

While the surfaces of the film is activated in the activating device (20), the unreacted fluorine escaping from the inlet (22) and the exit (23) is collected by the fluorine suction chambers (25), (25'), and then delivered to the collector pipe (30) of an exhaust fan (30) via pipes (26), (26'), (27), (27') and decontaminated.

The activated film (F) is coated by the water drop resistant through the applicator (40), and then dried by the drier (50) at a temperature of from 40 to 70°C. Hot air is transmitted to the hot air dispensing chambers (52), (52') at the lower end of the shell (51) via hot air feed pipes (53), (53'), and sprayed through the nozzles (54), (54') onto the coated surfaces of the film in a machine direction so as to dry the water drop resistant on the film.

In the above-described equipment for producing a water-drop-free synthetic resin film of the present invention, the calendering and conveying device (10) is directly connected to the applicator for the water drop resistant to make the

water-drop-free film. Besides, a non-water-drop-free film may be converted into a water-drop-free film only by an applicator for a water drop resistant.

#### Example 1

A polyethylene film having a thickness of 60 microns and a width of 32 cm is passed through a surface activating device at a speed of 2 m/min. The film is dip coated by a water drop resistant formed by mixing 0.5 gram of colloidal silica and propylene resin in 1 liter of water, as shown in FIG 4. The film is then dried at a temperature of 60 °C. The coating weight of the water drop resistant is about 0.2 g/m<sup>2</sup>.

#### Example 2

A polyethylene film having a thickness of 60 microns and a width of 32 cm is passed through a surface activating device at a speed of 5 m/min. The film is roll coated by a water drop resistant formed by mixing 1.5 gram of colloidal silica and propylene resin in 1 liter of water, as shown in FIG 1. The film is then dried at a temperature of 70 °C. The coating weight of the water drop resistant is about 0.5 g/m<sup>2</sup>.

#### Comparative Example 1

The water-drop-free film is made in the same manner as Example 2 except that the propylene resin is replaced by a vinyl acetate resin adhesive.

#### Analysis to the test results

The water-drop-free films prepared in Examples 1, 2 and Comparative Example 3 are tested in a water tank kept at 60 °C. The results are shown in Table 1. It is apparent that the water-drop-free films prepared according to the present invention exhibit a superior water drop resistance for a long period.

Table 1

Time type	1 day	10 days	30 days	60 days	180 days	360 days
Ex. 1	⊙	⊙	⊙	0	0	×
Ex. 2	⊙	⊙	⊙	⊙	⊙	⊙
Com. Ex. 1	⊙	0	Δ	×	×	×

Notes: ○ shows no water drops at all;

0 indicates that water drops are formed on 1/5 of the surface;

× indicates that water drops are formed on 1/2 of the surface.

As shown above, the durability of the water drop resistant is improved by a method for producing a water-drop-free synthetic resin film comprising activating the surface of the film with diluted fluorine gas and applying a water drop resistant composed of colloidal silicon dioxide and an aqueous propenyl resin to said activated surface of the film. The water drop resistance may be maintained for the whole service life of the film. In addition, the film has no potential of leakage of water drop resistant, so there is no harm to agriculture and horticulture crops.

Since the surface of a film is activated by fluorine in the equipment for producing the water-drop-free synthetic resin of the present invention, it is safe, cost effective, simple and may be used to make a wide film. In addition, the unreacted fluorine escaping during operation is collected and decontaminated, there is no air pollution.



What is claimed is:

1. A method for producing a water-drop-free synthetic resin film for agriculture and gardening use, comprising activating the surface of a calendared synthetic resin film with diluted fluorine gas, applying a water drop resistant composed of colloidal silicon dioxide and an aqueous propenyl resin to said activated surface of the film, and drying the film, to form a water-drop-free synthetic resin film.

2. The method according to claim 1, wherein said fluorine gas is diluted by one or more gas selected from the group consisting of air, nitrogen, argon, carbon dioxide and helium to a concentration of 1 to 5% by weight.

3. The method according to claim 1, wherein said water drop resistant is a dispersion of colloidal silicon dioxide and the aqueous propenyl resin in an aqueous or alcohol medium with a solid content of 0.1 to 35 % by weight.

4. The method according to claim 1, wherein said water drop resistant has a ratio of colloidal silicon dioxide to the aqueous propenyl resin in a range of 1:4 to 3:1.

5. An equipment for producing a water-drop-free synthetic resin film for agriculture and gardening use, comprising a calendaring and conveying device, a film surface activating device, an applicator for a water drop resistant, a vertical drier, and a film coiling wheel, said film surface activating device comprising a vertical hexahedral shell having a slot inlet on the top and a slot exit on the bottom of the shell, and fluorine supply pipes arranged on the both sides of the shell in a traverse direction.

6. The equipment according to claim 5, wherein fluorine suction chambers are installed near the inlet and exit, the pipes on the both sides of the chambers are communicated to a collector pipe which is connected to an exhaust fan having an exit equipped with a decontaminator.

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